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US 43 48 502

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(54) Thermoplastic elastomer composition

(57) Thermoplastic elastomer composition containing:

I) 5 to 60 wt%, in relation to the total weight of the thermoplastic and elastomer phase, of one or more thermoplastics chosen from the group consisting of polycarbonate (PC), polystyrene acrylonitrile (SAN), polymethyl methacrylate (PMMA), polyoxymethylene (POM), polybutylene terephthalate (PBT), polyamide (PA), and polyvinyl chloride (PVC), and

II) 40 to 95 wt%, in relation to the total weight of the thermoplastic and elastomer phase,

A) of a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt% produced by the emulsion polymerization technique and 0.01 to 0.5 wt% of one or more multiple ethylenically unsaturated monomer units from the group consisting of divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate, in each case in relation to the total weight of the copolymer, or

B) of a crosslinked, and if necessary functionalized, ethylene-vinyl ester graft copolymer produced by the emulsion polymerization technique made available by grafting 5 to 80 wt%, preferably 5 to 50 wt%, in relation to the total weight of the graft copolymer, of a comonomer phase made from:

a) 70 to 99.99 wt% of one or more monomers from the group consisting of esters of acrylic acid or methacrylic acid

and alcohols with 1 to 12 C atoms and the vinyl ester of non-branched or branched carboxylic acids with 1 to 12 C atoms,

b) 0.01 to 5 wt% of one or more multiple ethylenically unsaturated monomers γ chosen from the group consisting of divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate,

c) 0 to 25 wt% of one or more comonomers γ , which are substituted with or more carboxyl-, amide-, hydroxy-, amine-, sulfonate-, epoxy-, or silanol groups,

20 to 95 wt%, in relation to the total weight of the graft copolymer, of a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt%, in relation to the ethylene-vinyl ester copolymer,

whereby the elastomers of phase II) in each case are present in the form of spherical particles, with a median particle size of 0.1 to 5.0 μm , homogeneous in the thermoplastic matrix I).

Description

[0001]

The invention concerns thermoplastic elastomer compositions containing a thermoplastic polymer phase and an elastomer polymer phase, a technique for their production, and the elastomer used as an intermediate product for the production.

[0002]

Thermoplastic elastomers are characterised by the fact that they act as thermoplastics at temperatures above the softening temperature and as elastomers over a broad temperature range, exhibiting rubber-like, flexible characteristics. The advantages of thermoplastic elastomers consist, on the one hand, of the fact that the treatment technology is more economical in comparison to the rubber technology and, on the other hand, of the trouble-free reusability of the used TPE products and/or of production[-cost] decrease in the production of TPE products.

[0003]

For thermoplastic elastomers (TPE), their presence is characteristic both in phases with a predominantly thermoplastic behavior, and in phases with flexible [rubber] behavior. These phases can be formed by the purposeful selection of suitable monomers and the polymerization process with the resultant phase mixing, or by thermomechanical mixing of the thermoplastics and elastomers. The elastomer is in addition mixed into the thermoplast melt, whereby the elastomer phase is to be separated, during the mixing process, into particles and is distributed as homogeneously as possible in the melt. For the production of thermomechanically stable elastomer phases with, to a large extent, a defined elastomer particle structure in the thermoplastic elastomers, the elastomer phase, under the addition of a crosslinked component during the mixing process is formed by dynamic crosslinking in the thermoplast melt.

[0004]

A TPE composition made of a polyamide and ethylene-vinyl acetate rubber is discussed in USA 4348502, whereby the rubber component is crosslinked during mixing with the thermoplast melt by the addition of crosslinked or [sic] ethylene-vinyl acetate copolymers before the addition to the thermoplast melt, then crosslinked and cleaved. With this procedure, elastomers are crosslinked before the mixture with the thermoplastic component in an additional processing step. Since the crosslinked elastomer made available thereby is not applicable in the form of TPE's, it must be cleaved in a further additional processing step. It is therefore disadvantageous that the rubber component must be crosslinked and cleaved in additional processing steps before it can be used in TPE's. It is further disadvantageous that the construction of the hard and soft

phase on the desired order of magnitude is not accurately defined and that problems, caused by different crosslinking degrees, can occur, disturbing the production process.

[0005]

Thermoplastic elastomers based on a polyamide as the thermoplastic component and crosslinked polyacrylate-rubber as the elastomer component are described in EP-A 337977. Here likewise, with the above-mentioned disadvantages, dynamic vulcanizing [occurs]. Other TPE's based on a polyamide as the thermoplastic component and crosslinked polyacrylate rubber as the elastomer component are described in EP-A 321830 (USA 5075380).

[0006]

The invention has the basic objective to make thermoplastic elastomers available by thermomechanical mixing, without an additional crosslinking step and/or cleavage step, exhibiting a thermomechanically stable, well-defined elastomer phase structure and good mechanical characteristics, and with improved flexibility characteristics at higher temperatures.

[0007]

The objective is achieved by the development of a crosslinked ethylene-vinyl ester copolymer, without additional crosslinking. A cleavage step is easily carried out, with a dust-free form [if product] being producible and thus is easily manageable, and which exhibits a microparticle structure in a spherical shape after mixture with the thermoplastic component, which does not require further post-crosslinking, is cleavage-stable, and remains thermoplastic under ordinary treatment conditions.

[0008]

The subject of the invention involves a thermoplastic elastomer composition containing:

- I) 5 to 60 wt%, in relation to the total weight of the thermoplastic and elastomer phase, of one or more thermoplastics from the group consisting of polycarbonate (PC), polystyrene acrylonitrile (SAN), polymethyl methacrylate (PMMA), polyoxymethylene (POM), polybutylene terephthalate (PBT), polyamide (PA), and polyvinyl chloride (PVC), and
- II) 40 to 95 wt%, in relation to the total weight of the thermoplastic and elastomer phase, of a crosslinked ethylene-vinyl ester copolymer, made available by the emulsion polymerization of ethylene and vinyl ester monomers with multiple ethylenically unsaturated comonomers and, if necessary, following graft copolymerization.

[0009]

As thermoplastics, a polycarbonate, polyamide, or polyvinyl chloride is preferably used. Particularly preferably, polyamide PA 4,6 (polytetramethylene adipic acid amide), PA 6 (polycaprolactam), PA 6,6 (polyhexamethylene adipinamide), PA 6,10 (polyhexamethylene sebacic acid amide), PA 11 (polyaminoundecanoic acid), and PA 12 (polylaurin lactam) are used. Preferably, the TPE's contain a thermoplastic at 10 to 40 wt%, in relation to the total weight of the thermoplastic and elastomer phase.

[0010]

As the elastomer component II), suitably crosslinked ethylene-vinyl ester copolymers of vinyl esters of non-branched or branched carboxylic acids with 1 to 12 C atoms, for example, vinyl acetate, vinyl propionate, vinyl laurate, vinyl esters of α -branched carboxylic acids with 9 or 10 C atoms, and isopropenyl acetate are used. The ethylene content is 20 to 60 wt%, preferably 40 to 60 wt%, in each case in relation to the total weight of the ethylene-vinyl acetate copolymer. Crosslinked ethylene-vinyl acetate copolymers are preferred. Crosslinked ethylene-vinyl acetate copolymers with a median particle size of the elastomer primary particles being 0.1 to 5.0 μm are particularly preferential.

[0011]

In a preferential execution form, the crosslinked ethylene-vinyl ester copolymers are contained at 0.01 to 0.5 wt%, in relation to the total weight of the copolymer [and] multiple ethylenically unsaturated monomer units. Examples of this are divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate. Preferably, divinyl adipate and triallyl cyanurate are used.

[0012]

As the ethylene-vinyl ester copolymer, preferably a crosslinked, and functionalized if necessary, ethylene-vinyl ester graft copolymer is made by grafting 5 to 80 wt%, preferably 5 to 50 wt%, in relation to the total weight of the graft copolymer, of a comonomer phase made from:

- a) 70 to 99.99 wt% of one or more monomers from the group consisting of the esters of acrylic acid or methacrylic acid and alcohols containing 1 to 12 C atoms and the vinyl ester of a non-branched or branched carboxylic acid with 1 to 12 C atoms,
- b) 0.01 to 5 wt% of one or more multiple ethylenically unsaturated monomers,

c) 0 to 25 wt% of one or more, with substituted functional groups, of comonomers, used with 20 to 95 wt%, in relation to the total weight of the graft copolymer, of a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt%, in relation to the ethyl vinyl ester copolymer.

[0013]

Preferential monomers a) are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, 2-ethylhexyl acrylate, n-hexyl acrylate, vinyl laurate, or a vinyl ester of an α -branched carboxylic acid with 9 to 10 C atoms (VeoVa9^R, VeoVa10^R), in particular n-butyl acrylate and 2-ethylhexyl acrylate.

[0014]

As multiple ethylenically unsaturated monomers b), preferably divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate, in particular divinyl adipate and triallyl cyanurate, are used.

[0015]

In a preferential execution form, 0.01 to 25 wt% of monomers c) are inserted in the graft monomer phase. Preferential monomers c) are ethylenically unsaturated compounds with one or more carboxyl-, amide-, hydroxy-, amine-, sulfonate-, epoxy-, or silanol groups being substituted. Particularly preferentially acrylic acid, methacrylic acid, maleic acid, fumaric acid, acrylamide, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, vinyl sulfonate, 2-acrylamido-2-methylpropane sulfonate, vinyltrimethoxysilane, vinyltriethoxysilane, methacryloxypropyltrimethoxysilane, in particular (meth)acrylic acid, maleic acid, fumaric acid, vinyl sulfonate, and 2-acrylamido-2-methylpropane sulfonate, are used.

[0016]

The graft monomer phase preferably contains 93 to 98.9 wt% of one or more monomers a), 0.1 to 2.0 wt% of one or more monomers b), and 1 to 5 wt% of one or more monomers c), in each case in relation to the total weight of the graft monomer phase. In a preferential execution form the fraction of the graft comonomer phase is 5 to 50 wt%, in relation to the total weight of the grafting copolymer.

[0017]

As grafting basis the above-mentioned ethylene-vinyl ester copolymers are preferably used, ethylene-vinyl acetate copolymers. The ethylene-vinyl ester graft base preferably has an ethylene content of 40 to 60 wt%.

[0018]

A further subject of the invention are crosslinked ethylene-vinyl ester graft copolymers, available by grafting from 5 to 80 wt%, in relation to the total weight of the graft copolymer, of a comonomer phase made from:

- a) 70 to 99.98 wt% of one or more monomers from the group consisting of esters of acrylic acid or methacrylic acid and alcohols containing 1 to 12 C atoms and a vinyl ester of non-branched or branched carboxylic acids with 1 to 12 C atoms,
- b) 0.01 to 5 wt% of one or more multiple ethylenically unsaturated monomers,
- c) 0 to 25 wt% of one or more comonomers with substituted functional groups, along with 20 to 95 wt%, in relation to the total weight of the graft copolymer, of a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt%, in relation to the ethylene-vinyl ester copolymer.

[0019]

The production of the ethylene-vinyl ester copolymers preferably takes place via emulsion polymerization at a temperature of 30 to 90°C and ethylene pressures of 40-90 bar abs., in the presence of the usual ionic or nonionic emulsifying agents used for emulsion polymerization and using the water-soluble radical formers commonly used for emulsion polymerization. Suitable emulsifying agents and initiators are specified in the following in the description of the graft copolymerization. A suitable technique for the production is described, for example, in DE-A 37 43 142.

[0020]

The ethylene pressure set at the beginning of the polymerization and kept constant by accelerating [sic]. The addition of the comonomers is arbitrary. The vinyl ester comonomer is preferably used at 5 to 20 wt%; the remainder is metered in the process of the polymerization. The components of the initiator system are preferably proportioned [added in proportions]. The addition of the emulsifying agent is arbitrary; preferably, the emulsifying agent is partially used [initially] and the remainder is proportioned during the polymerization. The fixed content of the vinyl ester-ethylene copolymer latex is preferably 30 to 60 wt%.

[0021]

For the production of ethylene-vinyl ester graft copolymers, the crosslinked ethylene-vinyl ester copolymer preferably used is aqueous latex, with a fixed content of 20 to 50 wt%, and the graft monomer phase is grafted in the emulsion polymerization technique.

[0022]

The radical emulsion polymerization can be accomplished in the same way as ordinary polymerization in stirring-type reactors or under pressure in stirring autoclaves. The polymerization temperature is usually 20 to 110°C, preferably 30 to 80°C.

[0023]

For the introduction of the emulsion polymerization, a common radical former is used in an amount of preferably 0.01 to 3.0 wt%, in relation to the monomer phase. Examples of the radical former are ammonium and potassium peroxydisulfate; hydrogen peroxide; alkyl hydroperoxides such as t-butyl hydroperoxide; and potassium-, sodium-, and ammonium peroxydiphosphate. Initiation can take place either directly via a temperature rise or at low temperatures via the application of reducing agents. Suitable reducing agents are, for example, sodium formaldehyde sulfoxylate, sodium sulfite, sodium hydrogen sulfite, dithionite, or ascorbic acid, which can be used in an amount of preferably 0.01 to 0.5 wt%, in relation to the monomer phase.

[0024]

As dispersing agents, the ionic and nonionic emulsifying agents commonly used in emulsion polymerization can be used. Preferably, 0.1 to 10.0 wt% of emulsifying agent, in relation to the monomer phase, is used. Suitable emulsifying agents are, for example, anionic surfactants such as alkyl sulfates with a chain length of 8 to 18 C atoms, alkyl and alkylaryl ether sulfates with 8 to 18 C atoms, alkyl and alkylaryl ether sulfates with 8 to 18 C atoms in the hydrophobic residue and up to 40 ethylene or propylene oxide units, alkyl- or alkylaryl sulfonates with 8 to 18 C atoms, oleic acid sulfonate, and esters and hemi-esters of sulfosuccinic acid with monovalent alcohols or alkyl phenols. Suitable nonionic surfactants are, for example, alkylpolyglycol ethers or alkylaryl polyglycol ethers with 8 to 40 ethylene oxide units.

[0025]

If necessary, buffer substances such as sodium carbonate, sodium hydrogen phosphate, or alkali acetates can be used for polymerization.

[0026]

The polymerization can be continuous or intermittent, after the introduction of all or individual constituents of the reaction mixture or after partial introduction, then with the post-dosing in of individual constituents of the reaction mixture, or it can be performed in a dosing technique whereby only the ethylene-vinyl ester copolymer latex is used. In a preferential execution form, the graft monomer phase is proportioned [added in proportions] as an emulsion, which contains monomers, emulsifying agent and water along with the latex substance, whereby the initiator can be used together [with the other substances] or added separately. To lower the residual monomer content in a preferential execution form, a post-polymerization is carried out after conclusion of the dosing for 1 to 3 hours.

[0027]

For the separation of the elastomers, the latex is preferably coagulated, the water is separated, and the moist polymer is formed into a dust-free, easily formed powder with the grain size of the primary seed agglomerates being 50 to 3000 μm after the drying process.

[0028]

The precipitation can be accomplished with well-known techniques continuously, semi-continuously, or intermittently. As the precipitant, alkali-(NaCl, KCl), alkaline earth salts (MgCl_2 , MgSO_4 , Ca acetate), aluminum salts, acids, caustic solutions, and water-soluble polymers (polyvinyl alcohols, cellulose ether, and flocculants) can be used. One can also coagulate the dispersion without a precipitant, with only a temperature increase to 100°C at the most and shearing, i.e., by strong stirring or in homogenization mills. The coagulate is separated with filters, band filters, presses, decanters, or centrifuges.

[0029]

In the drying process, preferably an "anti-block" agent is added to the polymer at 2 to 20 wt%, in relation to the polymer weight. Suitable anti-block agents are highly dispersed silicic acid, chalk, silicates, bentonite, or fine-particle polymers such as polyvinyl chloride. For drying all ordinary drying devices, such as drum dryers, flow dryers, fluidized bed dryers, or drying furnaces, can be used.

[0030]

The elastomer is finally produced, without grinding, as a fine-particle, dust-free, easily formed powder from agglomerated elastomer primary particles. The median particle size of the elastomer primary particles is from 0.1 to 5.0 μm , preferably 0.2 to 1.0 μm .

[0031]

For production of the thermoplastic elastomers, the powdered elastomer component, without previous cleavage, is mixed with a powder or granulate-forming thermoplastic component. Additionally, ordinary additives used for plastics processing can be used in this step, for example, pigments, lubricants, stabilizers, filling materials, and softeners.

[0032]

The thermoplastic and elastomer can be proportioned in directly in this technical step, for example, with a compounding device, for example, a compounding extruder, over 2 dose-adjusting devices, and can be treated with the compounds by means of the usual techniques such as extruding, injection molding, or calendering.

[0033]

The thermoplastic elastomers according to the invention are suitable, for example, for the production of packing [caulking] films, or cushioning materials.

[0034]

With the available invention, elastomers are made available, which are produced in easily carried out and dust-free form, and exhibit a spherical microparticle structure, with a median particle size of 0.1 to 5.0 μm , and which is cleavage-stable and remains thermoplastic under the treatment conditions.

[0035]

During the production of blends from the thermoplastic hard component and elastomer phase, the particle structure (hard/soft phase construction) necessary for the [desired] TPE properties is made possible with, if necessary, thermomechanical mixing in ordinary compounding devices without additional adjustment, i.e., without post-crosslinking, which produces the elastomer phase. One thereby obtains--also without a crosslinking step in processing the mixture--thermoplastic elastomers with an accurately defined, thermomechanically stable hard/soft phase structure and with sufficient compatibility of the two phases: the elastomer phase is in the form of spherical particles, homogeneously distributed in the thermoplastic matrix.

[0036]

The following examples serve to further explain in the invention:

Production of the elastomer phase

Example 1

[0037]

In stirring autoclaves at 40°C under an ethylene pressure of 65 bar, a dispersion of vinyl acetate-ethylene copolymers (VAc/E) was produced. 1/10 of the vinyl acetate was present in the polymerization vessel. The remainder was added after the start of polymerization, while dosing [metering] over 8 h. Afterwards, this was post-reacted [sic] for 3 h, whereby the ethylene pressure was held at 65 bar for 1.5 h. As the emulsifying agent, 1.03%, for example, of VAc/E was used [with] diisohexyl sulfosuccinate (Aerosol MA from the Cyanamid Company), in the ratio of 1:4 in the vessel, and the dosage was divided. As the crosslinked component, 0.12%, in relation to VAc/E, of divinyl adipate was used in the ratio of 1:50 in the polymerization vessel, and the dosage was distributed [divided]. The reaction control was conducted in the usual way via the addition of 0.48% potassium peroxy disulfate and 0.11% sodium formaldehyde sulfoxylate, in each case based on VAc/E during the reaction period. The dispersion was stopped with a [regulated using] KOH solution to pH 5.5.

[0038]

For the isolation of the elastomer component, 0.5 wt% of a dispersion consisting of calcium acetate was added and heated under stirring at 80°C. The coagulate was drained on a filter and the filter cake was dried after the addition of 10 wt% chalk in a fluidized bed dryer.

[0039]

A powdered, freely flowing ethylene-vinyl acetate copolymer was obtained, with [consisting of] 44 wt% of ethylene units and 0.12 wt% of divinyl adipate units. The powder grain diameters were 50 to 3000 µm. The particle diameter of the primary particles was approximately. 0.27 µm.

Example 2

[0040]

In a stirring autoclave, 293 kg of a latex (fixed content 40%) of ethylene-vinyl acetate copolymers, with an ethylene content of 44 wt%, was produced according to the procedure of Example 1, and heated together with 0.1 g of Fe-ammonium sulfate under stirring to 45°C. After reaching this temperature, one pre-emulsion made from 40 kg of water, 0.5 kg of Mersolat K30, 2.5 kg of acrylic acid, 50 kg of n-butyl acrylate, and 88 g of allyl methacrylate as well as a solution made from 18 g of Brueggolit, were added into 0.5 L of water; also, a solution made from 25 g of potassium persulfate was added into 2 L of water. After conclusion of the dosing, this was stirred for 1 hour.

[0041]

The isolation of the elastomer component took place similarly to Example 1.

[0042]

A powdered, freely flowing grafting copolymer was obtained from 69 wt% of an ethylene-vinyl acetate phase and 31 wt% of a crosslinked and functionalized polybutyl acrylate phase, with 95.0 wt% of butyl acrylate units, 4.8 wt% of acrylic acid units, and 0.2 wt% of allyl methacrylate units. The powder grain diameter was 50 to 3000 μm . The particle size of the primary particles was approximately 0.30 μm .

Production of thermoplastic elastomers**[0043]**

In a Cokneter (MDK 46, Buss Company) at a mass temperature of 220°C, a speed of 300 rpm, and a metering rate (gravimetric dosing of the two components) of 20 kg/h, 80 parts by weight of the product of Example 1 or Example 2 and 20 parts by weight of polyamide 12 (Vestamid L 1940, Hüls AG) were compounded and granulated.

[0044]

The elastomer phase was present as a spherical particle structure, with a particle size of approximately 0.30 μm .

Application technology test**[0045]**

The compounds made from the elastomers of Examples 1 and 2 were rolled in each case on a rolling mill for 5 minutes at 190°C. From the roll-coating by 5-minute pressing at 195°C and a pressure of 5 N/mm², press plates were made. From the press plate, the test specimens for the application technology test were punched.

[0046]

The ultimate tensile strength and elongation at break were obtained in the traction test according to DIN 53455.

[0047]

Shore hardness A was obtained according to DIN 53505.

[0048]

The elasticity (compression set) was obtained according to DIN 53517 at 23°C and 100°C.

[0049]

The results of the test are summarized in Table 1:

Table 1

Sample	Example 1	Example 2
Shore hardness A	77	74
Ultimate tensile strength (N/mm ²)	6.1	7.1
Elongation at break (%)	131	147
Compression set (%)		
23°C	37	32
100°C	83	45

Patent claims

1. Thermoplastic elastomer composition containing:

I) 5 to 60 wt%, in relation to the total weight of the thermoplastic and elastomer phase, of one or more thermoplastics chosen from the group consisting of polycarbonate (PC), polystyrene acrylonitrile (SAN), polymethyl methacrylate (PMMA), polyoxymethylene (POM), polybutylene terephthalate (PBT), polyamide (PA), and polyvinyl chloride (PVC), and

II) 40 to 95 wt%, in relation to the total weight of the thermoplastic and elastomer phase,

A) a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt% produced by the emulsion polymerization technique and 0.01 to 0.5 wt% of one or more multiple ethylenically unsaturated monomer units chosen from the group consisting of divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate, in each case in relation to the total weight of the copolymer, or
B) a crosslinked, and if necessary functionalized, ethylene-vinyl ester graft copolymer produced by the emulsion polymerization technique made available by grafting from 5 to 80 wt%, preferably 5 to 50 wt%, in relation to the total weight of the graft copolymer, a comonomer phase made from:

a) 70 to 99.99 wt% of one or more monomers from the group consisting of esters of acrylic acid or methacrylic acid and alcohols with 1 to 12 C atoms and the vinyl ester of nonbranched or branched carboxylic acids with 1 to 12 C atoms,
 b) 0.01 to 5 wt% of one or more multiple ethylenically unsaturated monomers γ chosen from the group consisting of divinyl adipate, diallyl maleate, diallyl phthalate, allyl methacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylene glycol diacrylate, trimethylolpropane triacrylate, and triallyl cyanurate,
 c) in each case 0 to 25 wt% of one or more comonomers γ , which are substituted with one or more carboxyl-, amide-, hydroxy-, amine-, sulfonate-, epoxy-, or silanol groups and 20 to 95 wt%, in relation to the total weight of the graft copolymer, of a crosslinked ethylene-vinyl ester copolymer with an ethylene content of 20 to 60 wt%, in relation to the ethyl vinyl ester copolymer, whereby the elastomer phase II) is present in the form of spherical particles, with a median particle size of 0.1 to 5.0 μm , homogeneously distributed in the thermoplastic matrix I).

2. Thermoplastic elastomer composition according to Claim 1, characterized by the fact that as the elastomer component II), a crosslinked ethylene-vinyl acetate copolymer, with the median particle size of the elastomer primary particles being 0.1 to 5.0 μm , is used.
3. Thermoplastic elastomer composition according to Claims 1 to 2, characterized by the fact that as component I), polyamide PA 4,6 (polytetramethylene adipic acid amide), PA 6 (polycaprolactam), PA 6,6 (polyhexamethylene adipinamide), PA 6,10 (polyhexamethylene sebacic acid amide), PA 11 (polyaminoundecanoic acid), or PA 12 (polylaurin lactam) is used.
4. Thermoplastic elastomer composition according to one of Claims 1 to 3, characterized by the fact that 10 to 40 wt% of a thermoplastic, in relation to the total weight of the thermoplastic and elastomer phase, is contained.
5. Thermoplastic elastomer composition according to one of Claims 1 to 4, characterized by the fact that the graft monomer phase consists of 93 to 98.9 wt% of one or more monomers a), 0.1 to 2.0 wt% of one or more monomers b), and 1 to 5 wt% of one or more monomers c), in each case in relation to the total weight of the graft monomer phase.

6. Thermoplastic elastomer composition according to one of Claims 1 to 5, characterized by the fact that as monomers a), one or more monomers chosen from the group consisting of methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, 2-ethylhexyl acrylate, n-hexyl acrylate, vinyl laurate, or a versatic acid ester of alpha-branched carboxylic acids with 9 to 10 C atoms, are grafted.
7. Technique for the production of thermoplastic elastomers according to one of Claims 1 to 6, characterized by the fact that the powdered elastomer component II) is mixed with a powder or granulate-forming thermoplastic component I), without additional post-crosslinking, and treated with the usual techniques such as extruding, injection molding, or calendering.
8. Use of the thermoplastic elastomers according to one of Claims 1 to 6 for the production of packing [caulking] films, or cushioning materials.

Language Services Unit

Phoenix Translations

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